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Ionic Liquid-Mediated Dispersion and Support of Functional Molecules on Cellulose Fibers for Stimuli-Responsive Chromic Paper Devices

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Keywords

Cellulose, Paper, Supported ionic liquid, Composite, Stimuli-responsive materials

Abstract

Functional molecules play a significant role in the development of high-performance composite materials. Functional molecules should be well dispersed (ideally dissolved) and supported within an easy-to-handle substrate, to take full advantage of their functionality and ensure easy handling. However, simultaneously achieving the dissolution and support of functional molecules remains a challenge. Herein, we propose the combination of a nonvolatile ionic liquid and an easy-to-handle cellulose paper substrate for achieving this goal. First, the photochromic molecule, *i.e.* diarylethene, was dissolved in the ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([bmim]NTf₂). Then, diarylethene/[bmim]NTf₂ was supported on cellulose fibers within the paper, through hydrogen bonding between [bmim] cations of the ionic liquid and the abundant hydroxyl groups of cellulose. The as-prepared paper composites exhibited reversible, rapid, uniform, and vivid coloration and bleaching upon ultraviolet and visible light irradiation. The photochromic performance was superior to that of the paper prepared in the absence of [bmim]NTf₂. This concept could be applied to other functional molecules. For example, lithium perchlorate/[bmim] tetrafluoroborate supported within cellulose paper acted as a flexible electrolyte to provide a paper-based electrochromic device. These findings are expected to further the development of composite materials with high functionality and practicality.

1. Introduction

Functional molecules play a key role in materials development. For example, stimuli-responsive molecules, which can alter their chemical and/or physical properties in response to external stimuli, have received considerable attention as smart materials for diverse applications.¹⁻³ Among the various stimuli-responsive molecules, chromic molecules can change their colors upon various stimuli such as light, heat, or electrons.⁴ In particular, photochromic diarylethene and its derivatives have received much interest due to their thermal stability, rapid and reversible molecular switching, and fatigue resistance.⁵⁻⁷ They have been applied in devices such as actuators, photo-optical switches, optical memory, and displays.⁸

Functional molecules including diarylethene are often difficult to handle, due to their molecular-scale size. Thus, it can be desirable to support them on an easy-to-handle substrate. They should be well dispersed on the substrate, to suppress their aggregation and to take full advantage of their functionality. In this way, well-dispersed functional molecules, ideally being dissolved in some solvent, can be supported on substrates to obtain high-performance composite materials. However, there are challenges to achieving this. Most solvents cannot maintain the dissolution of solutes in an open system because of their evaporation.

Ionic liquids are organic salts with a melting point near or below room temperature.^{9,10} They are potential solvents for functional materials, because they are generally nonvolatile even under high-vacuum conditions.¹¹ Supported ionic liquids on solid substrates such as silica for catalytic applications have been reported.¹²⁻¹⁵ Among the many ionic liquids, 1-butyl-3-methylimidazolium ([bmim])-based ionic liquids can be supported on substrate materials with hydrogen-bond accepting ability, because [bmim] cations have hydrogen-bond donating ability.¹⁶ From this viewpoint, paper materials made from cellulose pulp fibers are promising substrates. Cellulose has abundant hydroxyl groups and thus excellent hydrogen-bond accepting ability, and paper is

inexpensive, lightweight, flexible, green, and sustainable. Paper can also serve as an effective substrate for stimuli-responsive chromic molecules, since most colors display well on white paper due to its high optical reflectance. A nonvolatile ionic liquid supported on cellulose pulp fibers within paper could be an effective media to dissolve functional molecules, including photochromic diarylethenes. This combination could provide high-performance composite materials with excellent functionality and handleability.

Herein, we report stimuli-responsive chromic paper devices. They were fabricated by supporting [bmim]-based ionic liquid on cellulose pulp fibers, and using the supported ionic liquid as a layer for dissolved photochromic diarylethene (Figure 1). Supporting the ionic liquid on cellulose fibers was achieved by room-temperature solution processes. The supported ionic liquid could in turn support dissolved diarylethene on the cellulose fibers of the paper. As proof-of-concept, the as-prepared paper device exhibited excellent photochromic performance with respect to color uniformity and vividness, which were significantly better than those of the paper device prepared without the ionic liquid. The nonvolatile ionic liquid ensured that the excellent photochromic performance remained largely unchanged over at least five years. The proposed strategy can be applied to various functional molecules. For example, lithium perchlorate (LiClO_4)/ionic liquid supported on paper was used as a flexible electrolyte to realize an all paper-based electrochromic device.

2. Experimental Section

2.1 Materials

Cellulose filter paper (ADVANTEC No. 5A, content of α -cellulose: >99 wt.%, thickness: ca. 200 μm) was purchased from Toyo Roshi Kaisha, Ltd., Tokyo, Japan and was cut into circular-shaped pieces (ca. 90 mg, 33 mm in diameter) before use. Cellulose nanofibers were prepared from

softwood chips (Japanese cedar, *Cryptomeria japonica*), according to a previous report.¹⁷ Three types of [bmim]-based ionic liquids, *i.e.* [bmim] tetrafluoroborate (BF₄) (98.0% purity), [bmim] hexafluorophosphate (PF₆) (98.0% purity), and [bmim] bis(trifluoromethanesulfonyl)imide (NTf₂) (98.0% purity), were obtained from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. Two types of photochromic diarylethene, *i.e.* 1,2-bis[2-methylbenzo[*b*]thiophen-3-yl]-3,3,4,4,5,5-hexafluoro-1-cyclopentene (>97.0% purity) and 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene (>98.0% purity) were purchased from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. Tetrahydrofuran (99.5% purity) and isopropyl ether (>99.0% purity) were purchased from Wako Pure Chemical Industries, Ltd., Tokyo, Japan, and Tokyo Chemical Industry Co., Ltd., Tokyo, Japan, respectively. An aqueous dispersion of poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT:PSS, Clevios P HC V4) was purchased from Heraeus Holding GmbH, Hanau, Germany. LiClO₄ (98.0% purity) was obtained from Wako Pure Chemical Industries, Ltd., Tokyo, Japan. All other chemicals were of reagent grade and were used without further purification.

2.2 Preparation of ionic liquid supported within cellulose paper substrate

[Bmim]-based ionic liquid (0.24 mmol) was dissolved in tetrahydrofuran (10 mL). Then, a piece of cellulose filter paper was immersed in the resulting solution, followed by evaporation of tetrahydrofuran at room temperature in a draft chamber. The obtained paper was thoroughly washed with isopropyl ether to remove excess ionic liquid, and was then vacuum-dried at room temperature. The ionic liquid content of the paper was calculated by weight variation.

2.3 Preparation and evaluation of photochromic paper device

Diarylethene (12 μmol) and [bmim]NTf₂ (0.24 mmol) were dissolved in tetrahydrofuran (10 mL). Then, a piece of cellulose filter paper was immersed in the resulting solution, followed by evaporation of tetrahydrofuran at room temperature in a draft chamber. The obtained paper was vacuum-dried at room temperature. The diarylethene content of the paper was measured as follows. Residual diarylethene, which was not supported within the paper, was first dissolved in diethyl ether, and was then quantified by ultraviolet-visible (UV-vis) absorption analysis using a U-670 spectrophotometer (JASCO Corp., Tokyo, Japan) (see Supporting Information, Figure S1). The amount of diarylethene supported within the paper was estimated by subtraction. To evaluate the photochromic performance, the color difference of the paper was measured using a color difference meter (CHROMA METER CR-400, Konica Minolta, Inc., Tokyo, Japan) before and after UV irradiation (UV lamp, wavelength: 312 nm, light intensity: 110 $\mu\text{W cm}^{-2}$) and visible irradiation (neutral white lamp, light intensity: 100 $\mu\text{W cm}^{-2}$).

2.4 Preparation and evaluation of electrochromic paper device

LiClO₄ and [bmim]BF₄ supported on cellulose pulp fibers within paper (denoted LiClO₄/[bmim]BF₄@paper) and PEDOT:PSS-coated cellulose nanofiber paper (denoted PEDOT:PSS@nanopaper) were used as an electrolyte and a transparent electrochromic electrode, respectively. The electrochromic paper device was fabricated using two pieces of PEDOT:PSS@nanopaper and one piece of LiClO₄/[bmim]BF₄@paper. In this case, the LiClO₄/[bmim]BF₄@paper was prepared as follows. [Bmim]BF₄ (0.88 mmol) and LiClO₄ (0.14 mmol) were dissolved in tetrahydrofuran (10 mL). Then, a piece of cellulose filter paper (25 mm \times 35 mm) was immersed in the resulting solution, followed by evaporation of the tetrahydrofuran at room temperature in a draft chamber. The PEDOT:PSS@nanopaper was prepared similarly to our previous report.¹⁸ Briefly, an aqueous suspension of cellulose nanofibers (0.3 wt.%, 50 mL)

was first dewatered on a membrane filter (A010A090C, mixed cellulose ester membrane, 0.1 μm pore diameter, Advantec Toyo Kaisha, Ltd., Tokyo, Japan) by suction filtration. Then, an aqueous dispersion of PEDOT:PSS with electrochromic properties (0.008 wt.%, 15 mL) was added and filtered in the same manner, followed by hot-pressing at 110 $^{\circ}\text{C}$ for 7 min (1.1 MPa), and subsequent peeling from the membrane. The PEDOT:PSS@nanopaper obtained (75 mm in diameter) was cut into rectangular-shaped pieces (30 mm \times 35 mm) before use. To fabricate the electrochromic paper device, the as-prepared $\text{LiClO}_4/[\text{bmim}]\text{BF}_4$ @paper (25 mm \times 35 mm) was sandwiched between two PEDOT:PSS@nanopapers (30 mm \times 35 mm), using double-sided tape (NW-40, Nichiban, Tokyo, Japan). Demonstration of the electrochromic paper device was conducted using a compact DC power supply unit (PMC110-0.6A, KIKUSUI ELECTRONICS Corp., Yokohama, Japan) at a voltage of 2.0 V and a current of 0.06 A.

2.5 Analyses

Surface observations were conducted using a field-emission scanning electron microscope (FE-SEM, S-4800, Hitachi High-Tech Science Corp., Tokyo, Japan) with an attached energy dispersive X-ray apparatus (EDX, EMAX ENERGY, Horiba Ltd., Kyoto, Japan). Paper samples without ionic liquid were subjected to FE-SEM analysis after sputter coating with osmium. Paper samples with ionic liquid were subjected to FE-SEM/EDX analysis without sputtering. Fourier transform infrared attenuated total reflection (FT-IR/ATR) spectra were obtained using a FT/IR-6100 instrument (JASCO Corp., Tokyo, Japan). X-ray diffraction (XRD) patterns were recorded using a Rigaku RINT 2000 diffractometer with Ni-filtered $\text{Cu } K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) with a scanning angle (2θ) range of 10–30 $^{\circ}$, at 40 kV and 40 mA. The crystallinity index of cellulose I was estimated from the (200) reflection ($2\theta = \text{ca. } 22.6^{\circ}$) according to the reported method.^{19,20} The tensile strength and Young's modulus of the papers were evaluated at 23 $^{\circ}\text{C}$ and 50% relative

humidity, using a Shimadzu EZ-TEST instrument equipped with a 500 N load cell (pulling rate: 1.0 mm min⁻¹, span length: 10 mm). The volume resistivity was measured using a LORESTA-EP instrument (MCP-T360, Mitsubishi Chemical Analytech, Co., Ltd., Kanagawa, Japan) or a HIRESTA-UX instrument (MCP-HT800, Mitsubishi Chemical Analytech, Co., Ltd., Kanagawa, Japan).

3. Results and discussion

3.1 Preparation of supported ionic liquid within cellulose fiber paper

Supporting ionic liquids on cellulose pulp fibers within paper was achieved using room-temperature solution processes. [Bmim]-based ionic liquids used in this study were highly viscous, leading to inconvenience for the supporting process. Therefore, tetrahydrofuran with low viscosity and high volatility was used as a solvent for the ionic liquids. First, the ionic liquid [bmim]NTf₂ was dissolved in tetrahydrofuran. Cellulose filter paper (α -cellulose content: >99 wt.%) was then soaked in this solution, after which the tetrahydrofuran was allowed to evaporate within 30 min. The resulting paper was washed with isopropyl ether to remove excess [bmim]NTf₂, and was then thoroughly dried under vacuum conditions. Figure 2 shows optical and FE-SEM/EDX images of the as-prepared paper. The appearance and porous structure of the paper remained almost unchanged before and after [bmim]NTf₂ treatment (Figures 2a and c). However, the rough surfaces of the cellulose pulp fibers became smoother after [bmim]NTf₂ treatment (Figures 2b and d). EDX mapping images of F, derived from [bmim]NTf₂, verified that [bmim]NTf₂ was supported on the entire surface of the cellulose pulp fibers within the paper (Figures 2e and f). FT-IR/ATR analysis also confirmed the presence of the characteristic peaks of [bmim]NTf₂^{21,22} (Figure 3a), indicating the existence of [bmim]NTf₂ on the cellulose pulp fibers. While ionic liquids such as [bmim]Cl have been frequently used as an efficient solvent for cellulose, [bmim]NTf₂ has almost no

cellulose-dissolving capacity^{23,24}. In the current study, there were no significant changes in the crystal structure of native cellulose (cellulose I)²⁵ before and after [bmim]NTf₂ treatment (Figure 3b). Then, the crystallinity index of cellulose I was slightly decreased from ca. 90% to 80% after [bmim]NTf₂ treatment. These results suggested that [bmim]NTf₂ was supported on the surfaces of cellulose fibers without large changes in the crystal structure of cellulose I. Table 1 shows selected physical and electrical properties of the as-prepared paper, denoted [bmim]NTf₂@paper. The [bmim]NTf₂ content was 2.25 mmol g-cellulose⁻¹ (48.5 wt.%). The mass concentration of [bmim]NTf₂ in the paper was ca. 497 kg m⁻³. The [bmim]NTf₂@paper exhibited improved electrical conductivity compared with the original paper. The volume resistivity of the paper decreased from 2.7×10^{13} to $8.3 \times 10^2 \Omega \text{ cm}$, indicating the entire coating of the paper with ionic conductive [bmim]NTf₂. The Young's modulus and tensile strength of the cellulose paper decreased from 0.34 GPa and 5.49 MPa to 0.21 GPa and 2.88 MPa, respectively, after supporting [bmim]NTf₂, possibly due to permeation of [bmim]NTf₂ into the interfaces between cellulose pulp fibers. However, the [bmim]NTf₂@paper retained sufficient physical strength for easy handling.

The supporting of [bmim]NTf₂ onto the entire surface of the cellulose pulp fibers (Figures 2c-f) was attributed to the hydrogen bonding between [bmim]NTf₂ and cellulose (Figure 1). It has been reported that [bmim] cations possesses hydrogen-bond donating ability,¹⁶ and cellulose with its abundant hydroxyl groups possesses hydrogen-bond accepting ability. Furthermore, [bmim]BF₄ and [bmim]PF₆ were also supported on cellulose paper in the same way as [bmim]NTf₂ (see Supporting Information, Figures S2-3 and Table S1). Thus, it was suggested that [bmim] cations play an important role in supporting of the ionic liquid on cellulose paper due to their hydrogen-bond donating ability. When these papers were immersed in polar solvents such as water, ethanol, dimethylformamide, and tetrahydrofuran, the supported ionic liquids desorbed from the cellulose paper. These results suggested that the polar surface of cellulose pulp fibers was compatible with

the polar solvent, leading to penetration of the solvent into interfaces between the ionic liquid and cellulose pulp fibers. The supported ionic liquids largely remained adsorbed on the cellulose pulp fibers under atmospheric conditions and when immersed in non-polar solvents such as diethyl ether, isopropyl ether, toluene, and hexane.

3.2 Photochromic paper device

[Bmim]NTf₂ supported on the entire surface of cellulose pulp fibers could potentially serve as a dissolving layer for functional molecules, which could in turn provide the cellulose paper with excellent functionality (Figure 1). To demonstrate this concept, a photochromic diarylethene was used as a model functional molecule. Specifically, 1,2-bis[2-methylbenzo[*b*]thiophen-3-yl]-3,3,4,4,5,5-hexafluoro-1-cyclopentene exhibits reversible pink-red coloration/decoloration by UV/visible light-induced switching of its molecular structure.²⁶ Many researchers have previously reported photochromism in ionic liquids.²⁷ As shown in Figure 4, the diarylethene/[bmim]NTf₂ mixture exhibited uniform and reversible color switching from almost colorless to pink upon UV and visible light irradiation. This suggested that diarylethene was dissolved in [bmim]NTf₂, and thereby showed effective photochromism. Despite such good photochromic properties, the [bmim]NTf₂ solution of diarylethene was very difficult to handle due to its viscous liquid form. Therefore, the diarylethene/[bmim]NTf₂ solution was supported on cellulose pulp fibers contained within the easy-to-handle solid cellulose paper. The procedure was as follows. Diarylethene and [bmim]NTf₂ were dissolved in tetrahydrofuran, followed by soaking of the cellulose paper in the solution and then the evaporation of tetrahydrofuran. Figure 5 shows the photochromic performances of diarylethene supported within the original paper without [bmim]NTf₂ (denoted as diarylethene@paper) and in the [bmim]NTf₂@paper (denoted as diarylethene/[bmim]NTf₂@paper). Their photochromic performances were quantitatively

evaluated using a color difference meter. While diarylethene exhibits photochromism even in the solid crystalline state,⁸ diarylethene@paper exhibited poor photochromic performance. The change in color of the solid-state diarylethene within the original paper was dull, even after UV irradiation for 20 s (Figures 5a and c). In comparison, the diarylethene/[bmim]NTf₂@paper exhibited a uniform and vivid pink color (Figures 5b and d). The color difference value of the diarylethene/[bmim]NTf₂@paper was 36.48 after UV irradiation for 20 s, which was 2.5 times higher than that of the diarylethene@paper (14.58). As shown in Figure 5g, the diarylethene/[bmim]NTf₂@paper exhibited second-scale rapid coloration upon UV irradiation, and its color difference value reached 50 at an UV irradiation time of 90 s. The saturated color-difference value of the diarylethene/[bmim]NTf₂@paper was also much higher than that of the diarylethene@paper. It should be noted that the diarylethene content was the same in each case, and that [bmim]NTf₂ itself did not exhibit photochromism. Therefore, the photochromic performance of diarylethene within the cellulose paper was significantly improved by the presence of the ionic liquid [bmim]NTf₂. FE-SEM observations suggested that [bmim]NTf₂ assisted the homogeneous dispersion of diarylethene molecules on the cellulose pulp fibers within the paper (Figure 5f), while diarylethene aggregated in the absence of [bmim]NTf₂ (Figure 5e). Thus, the well-dispersed diarylethene in [bmim]NTf₂, which was supported within the paper, would allow efficient UV-induced molecular switching, due to its lower steric hindrance compared with solid crystalline diarylethene. Thus, the resulting system achieved both excellent photochromic performance and practical utility.

The diarylethene/[bmim]NTf₂@paper exhibited rapid and reversible coloration and decoloration upon UV and visible light irradiation, respectively, over at least 10 cycles (Figures 5g and h). The excellent photochromic performance was maintained even after storing without any packaging at atmospheric conditions for at least five years, which was attributed to the nonvolatility and stability

against moisture of [bmim]NTf₂. As shown in Figure S4, photo-patterned coloration and various coloration such as blue and purple were also demonstrated. In summary, the diarylethene/[bmim]NTf₂@paper constitutes a new type of photo-responsive paper composite, and has various potential applications such as photo-writable and photo-erasable displays and UV sensors.

3.3 Electrochromic paper device

To demonstrate the versatility of our strategy, we investigated other combinations of functional molecules and [bmim]-based ionic liquids. LiClO₄ has been widely used as electrolytes in various electronic applications.^{28,29} In this study, a [bmim]BF₄ solution of LiClO₄ was supported within cellulose paper in a similar manner to diarylethene, to provide an easy-to-handle paper electrolyte. An electrochromic paper device was then fabricated by sandwiching the as-prepared LiClO₄/[bmim]BF₄@paper electrolyte between electrochromic conductive PEDOT:PSS-coated transparent cellulose nanofiber papers (denoted as PEDOT:PSS@nanopapers) as transparent electrochromic electrodes (Figure 6a). The PEDOT:PSS@nanopaper, which had a sheet resistance of ca. 1000 Ω square⁻¹ and an optical transmittance of ca. 70% at a wavelength of 550 nm, was prepared similarly to our previous report.¹⁸ As shown in Figures 6b and c, the device exhibited an electrically responsive color change from light blue to dark blue at an operating voltage and current of 2.0 V and 0.06 A, respectively, even when it was manually bent. It has been reported that PEDOT:PSS appears as light blue or dark blue in its oxidized or reduced state, respectively. PEDOT:PSS-based electrochromic displays can operate through electronically-induced ion transfer from electrolytes to the PEDOT:PSS electrodes.^{30–32} Therefore, it was suggested that the LiClO₄/[bmim]BF₄@paper could serve as a flexible electrolyte. As shown in Figures 6d and e, dolphin-patterned electrochromism was demonstrated using the patterned

PEDOT:PSS@nanopaper electrode. In summary, the LiClO₄/[bmim]BF₄@paper is a promising electrolyte material for realizing all paper-based flexible electrochromic displays.

4. Conclusion

We demonstrated the supporting of [bmim]-based ionic liquids within easy-to-handle cellulose paper, and used the supported ionic liquids as a dissolving layer for functional molecules such as photochromic diarylethene and LiClO₄ electrolyte. The diarylethene/[bmim]NTf₂@paper exhibited rapid, uniform, and vivid coloration/decoloration upon UV/visible light irradiation; the photochromic performance was significantly improved by the presence of [bmim]NTf₂. In addition, LiClO₄/[bmim]BF₄@paper acted as a flexible electrolyte for a paper-based electrochromic device. Thus, this approach could provide new types of paper displays such as photochromic and electrochromic paper devices.

Importantly, the paper-supported ionic liquids allowed the homogeneous dispersion and support of functional molecules to be achieved simultaneously. This led to excellent functionality and handleability of the paper devices. This strategy can be extended to various functional molecules, and these findings will further the development of high-performance and easy-to-handle functional composites.

Supporting Information

UV-vis absorption spectrum of diethyl ether solution of diarylethene, 1,2-bis[2-methylbenzo[b]thiophen-3-yl]-3,3,4,4,5,5-hexafluoro-1-cyclopentene; FE-SEM and EDX F element mapping images of cellulose paper after supporting of [bmim]BF₄ or [bmim]PF₆; FT-IR/ATR spectra and XRD patterns of cellulose paper before and after treatment with [bmim]BF₄

or [bmim]PF₆; ionic liquid content, and electrical and physical properties of the [bmim]BF₄@paper and [bmim]PF₆@paper; optical images of photochromic paper displays.

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Author Contributions

H. K. planned this study and prepared the manuscript. Experiments were carried out by H. K. H. K., M. N. and A. I. analyzed the results and discussed the manuscript during its preparation. All authors discussed the results and implications, and commented on the manuscript at all stages.

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Notes

The authors declare no competing financial interests.

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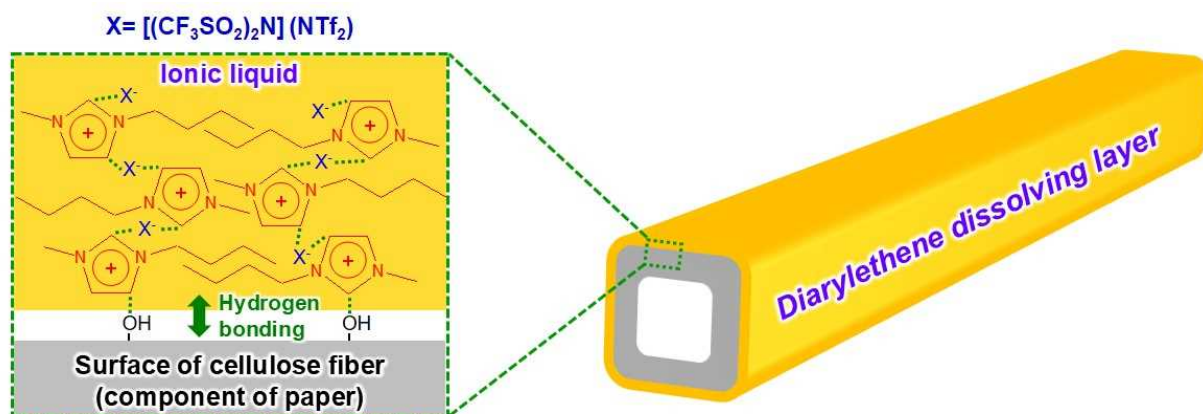


Figure 1. Schematic illustration of the supported ionic liquid [bmim]NTf₂ as a dissolving layer for photochromic diarylethene on cellulose pulp fibers.

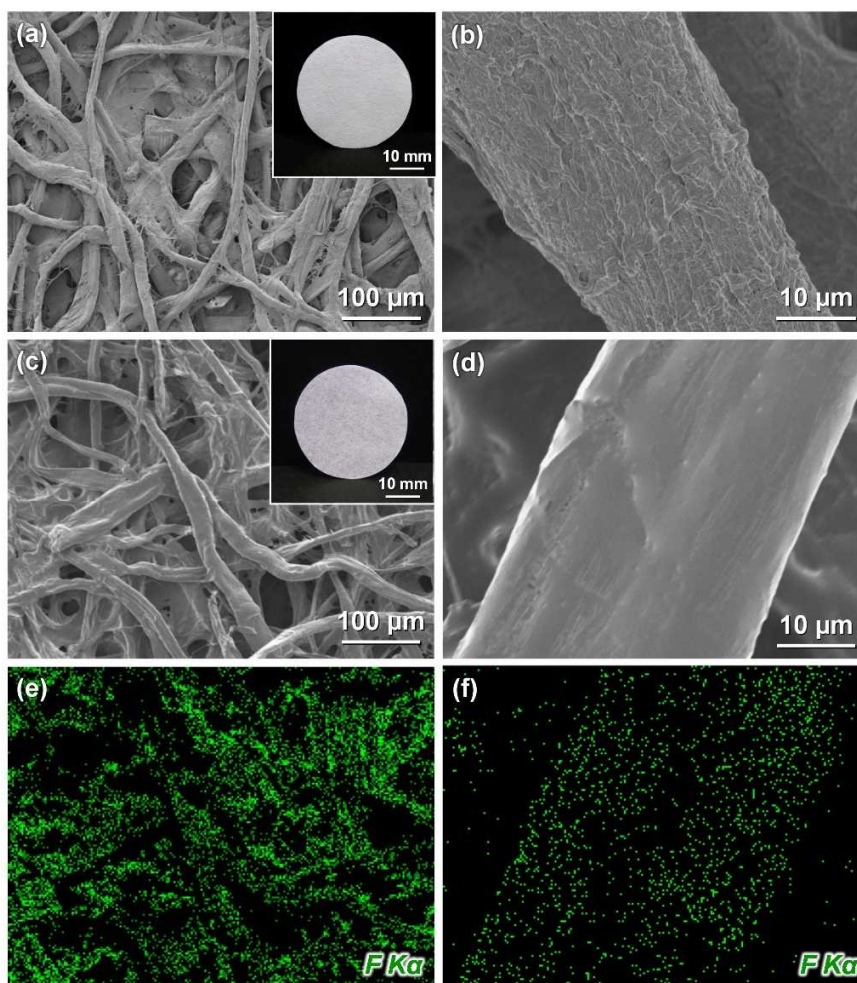


Figure 2. Cellulose filter paper before and after supporting of ionic liquid [bmim]NTf₂. (a) Optical and FE-SEM images of original cellulose paper, and (b) FE-SEM image of cellulose pulp fiber within the paper. (c) Optical and FE-SEM images of cellulose paper after [bmim]NTf₂ treatment, (d) FE-SEM image of cellulose pulp fiber within the paper, and (e, f) EDX F element mapping images of (c) and (d), respectively.

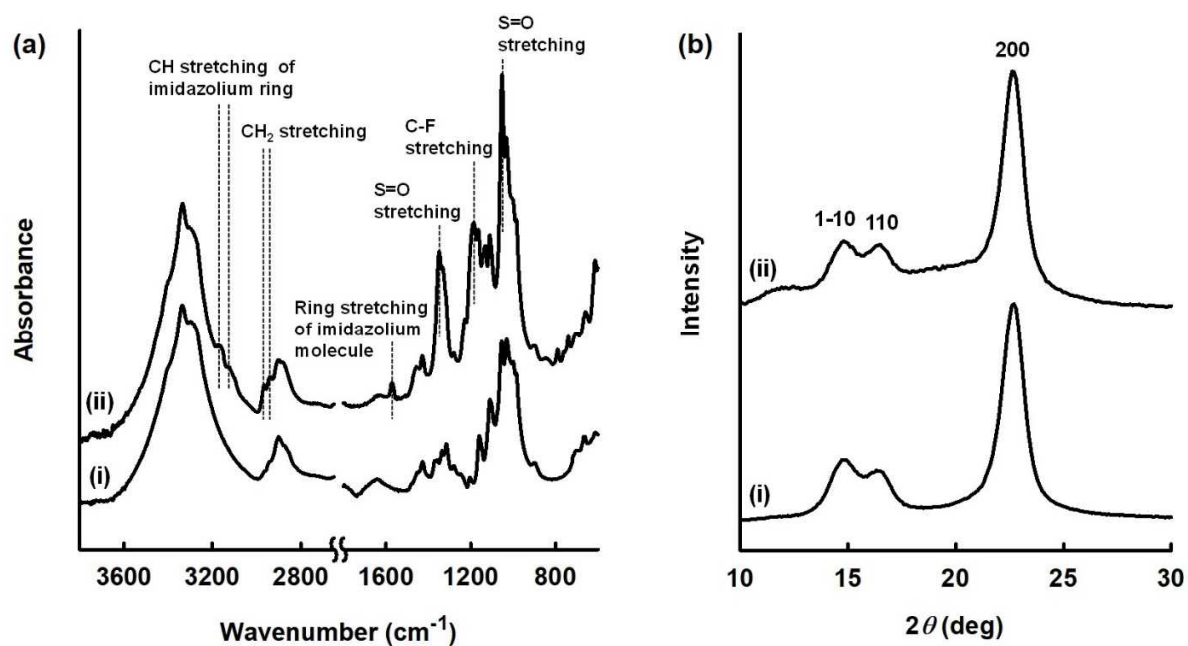


Figure 3. Characterization of cellulose filter paper before and after the supporting of [bmim]NTf₂. (a) FT-IR/ATR spectra and (b) XRD patterns of cellulose paper (i) before and (ii) after [bmim]NTf₂ treatment.

Table 1. Ionic liquid content, and electrical and physical properties of the original paper and [bmim]NTf₂@paper

	Ionic liquid content (mmol g-cellulose ⁻¹)	Volume resistivity ($\Omega \cdot \text{cm}$)	Young's modulus (GPa)	Tensile strength (MPa)
Original paper	-	2.7×10^{13}	0.34 ± 0.03	5.49 ± 0.36
[Bmim]NTf ₂ @paper	2.25 ± 0.06	8.3×10^2	0.21 ± 0.04	2.88 ± 0.39

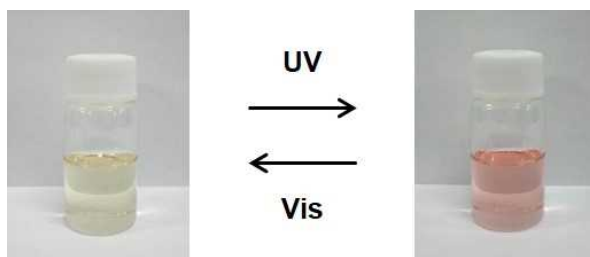


Figure 4. Optical images of the photochromic diarylethene 1,2-bis[2-methylbenzo[*b*]thiophen-3-yl]-3,3,4,4,5,5-hexafluoro-1-cyclopentene/[bmim]NTf₂ mixture after irradiation by UV and visible light. Diarylethene concentration: 50 μ M.

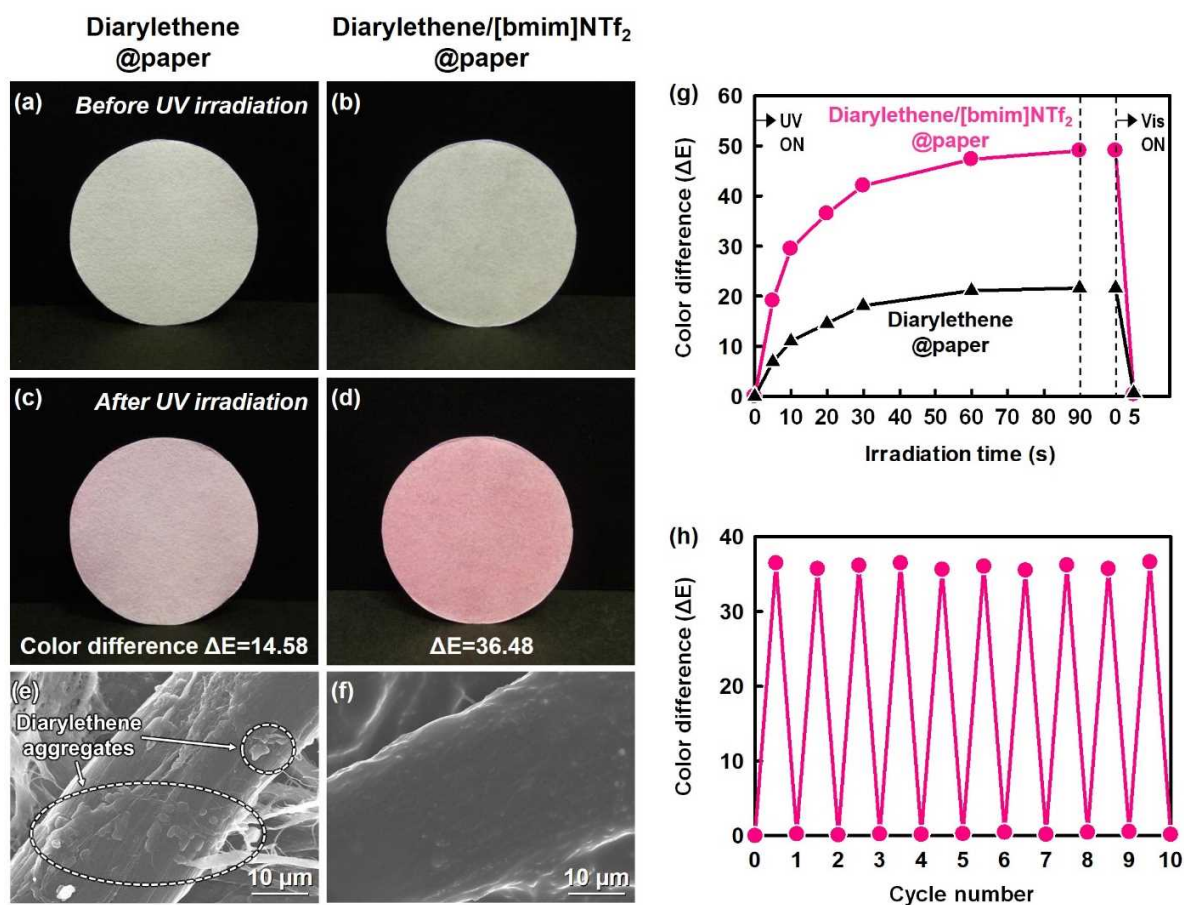


Figure 5. Photochromic performance of the diarylethene@paper with and without [bmim]NTf₂. Optical images of the (a, c) diarylethene@paper and (b, d) diarylethene/[bmim]NTf₂@paper (a, b) before and (c, d) after UV irradiation for 20 s. FE-SEM images of diarylethene on cellulose pulp fiber within the (e) original paper and (f) [bmim]NTf₂@paper. (g) Color difference values versus UV and visible light irradiation time for the diarylethene@paper and diarylethene/[bmim]NTf₂@paper, and (h) change in color difference values for the diarylethene/[bmim]NTf₂@paper upon alternate irradiation by UV (20 s) and visible light (5 s). Paper size: 33 mm in diameter. Diarylethene content: ca. 11 μmol . [Bmim]NTf₂ content: ca. 0.2 mmol. UV light: wavelength of 312 nm, light intensity of 110 $\mu\text{W cm}^{-2}$. Visible light: neutral white lamp, light intensity of 100 $\mu\text{W cm}^{-2}$.

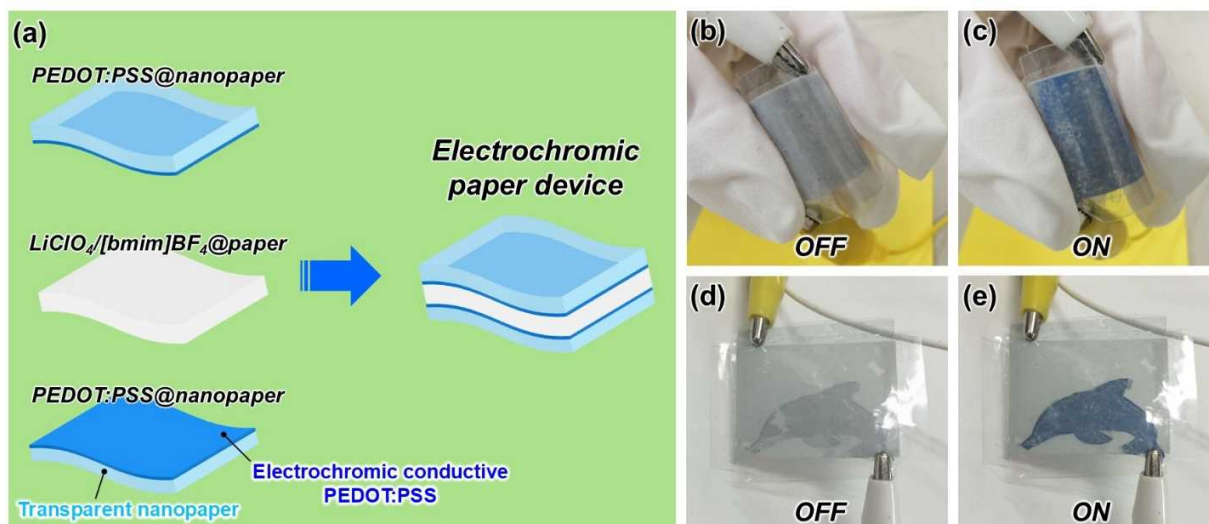
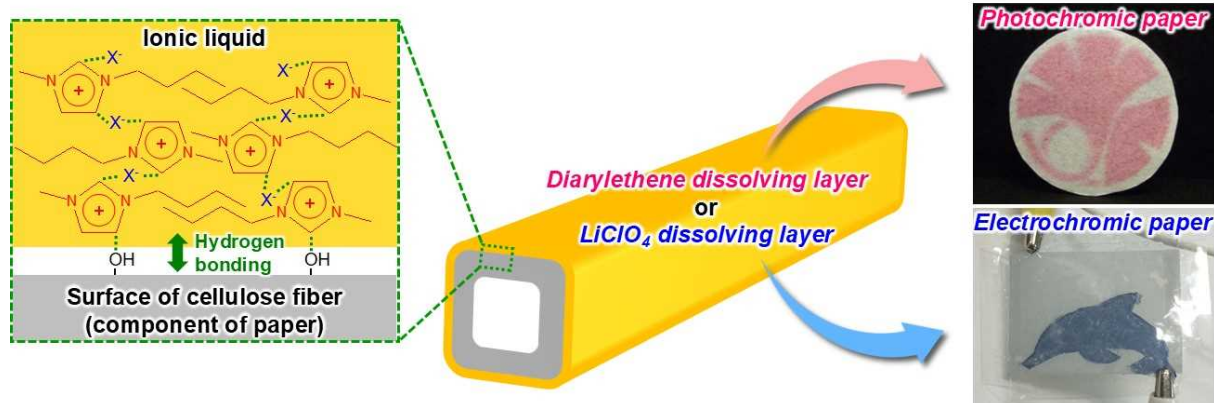


Figure 6. Electrochromic paper device. (a) Schematic illustration of the electrochromic paper device fabricated using two pieces of PEDOT:PSS@nanopaper and one piece of $\text{LiClO}_4/[\text{bmim}]\text{BF}_4@\text{paper}$ as transparent electrochromic electrodes and an electrolyte, respectively, (b, c) flexibility and corresponding performance of the electrochromic paper device, (d, e) dolphin-patterned electrochromism of the paper device. Operating voltage and current were 2.0 V and 0.06 A, respectively.

Table of Contents Graphic



Supporting Information

Ionic Liquid-Mediated Dispersion and Support of Functional Molecules on Cellulose Fibers for Stimuli-Responsive Chromic Paper Devices

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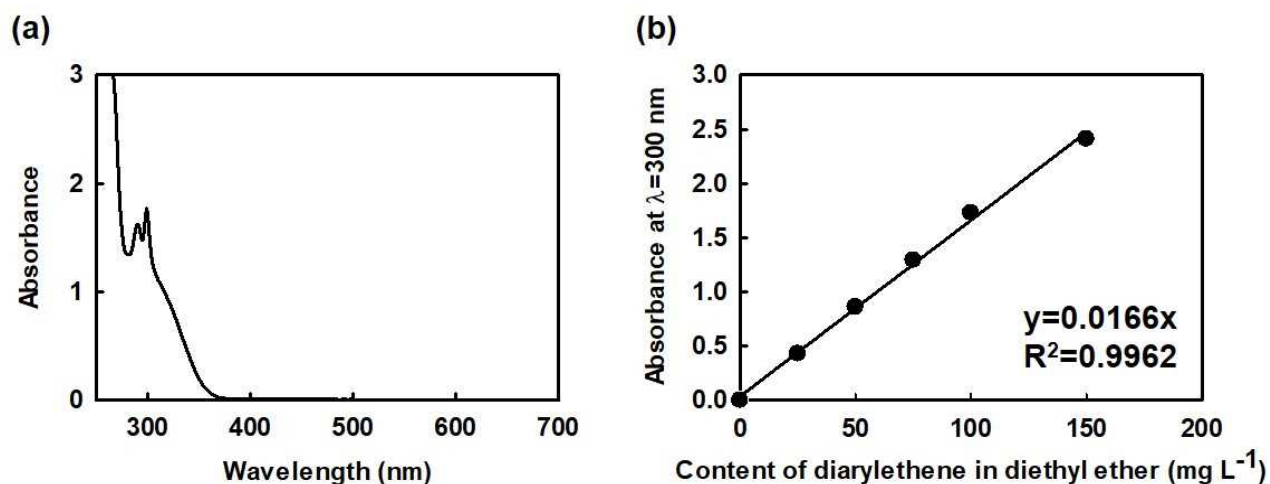


Figure S1. (a) UV-vis spectrum of diethyl ether solution of diarylethene, 1,2-bis[2-methylbenzo[b]thiophen-3-yl]-3,3,4,4,5,5-hexafluoro-1-cyclopentene (100 mg L^{-1}), and (b) absorbance at a wavelength of 300 nm versus content of 1,2-bis[2-methylbenzo[b]thiophen-3-yl]-3,3,4,4,5,5-hexafluoro-1-cyclopentene in diethyl ether.

As shown in Figure S1b, there was a proportional relationship ($y=0.0166x$) with a high coefficient of determination ($R^2=0.9962$) between the absorbance at 300 nm (y) and content of diarylethene in diethyl ether (x). The diarylethene content in the paper was measured as follows. Residual diarylethene, which was not supported within the paper, was thoroughly dissolved in diethyl ether, and was then quantified by the absorbance at 300 nm. The amount of diarylethene supported within the paper was estimated by subtraction.

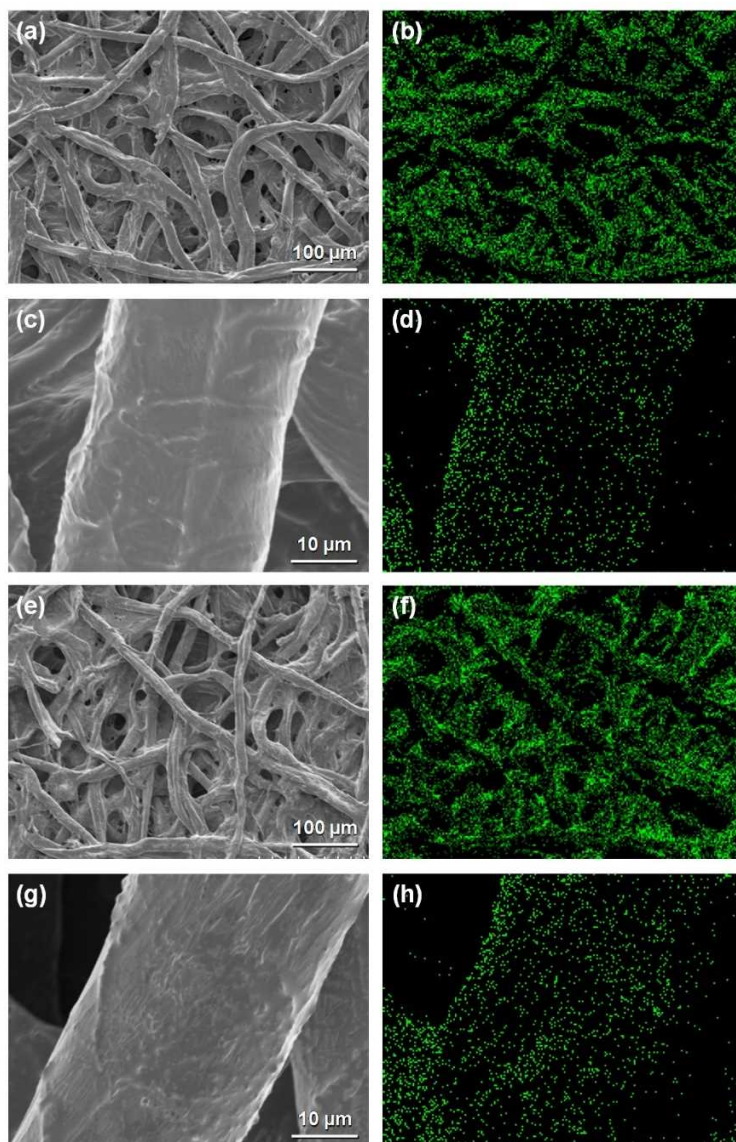


Figure S2. Cellulose filter paper before and after the supporting of [bmim]BF₄ or [bmim]PF₆. (a, c) FE-SEM images and (b, d) corresponding EDX F element mapping images of the [bmim]BF₄@paper. (e, g) FE-SEM images and (f, h) corresponding EDX F element mapping images of the [bmim]PF₆@paper.

As with [bmim]NTf₂ (Figure 2), [bmim]BF₄ and [bmim]PF₆ were also supported on the entire surface of the cellulose pulp fibers within the paper.

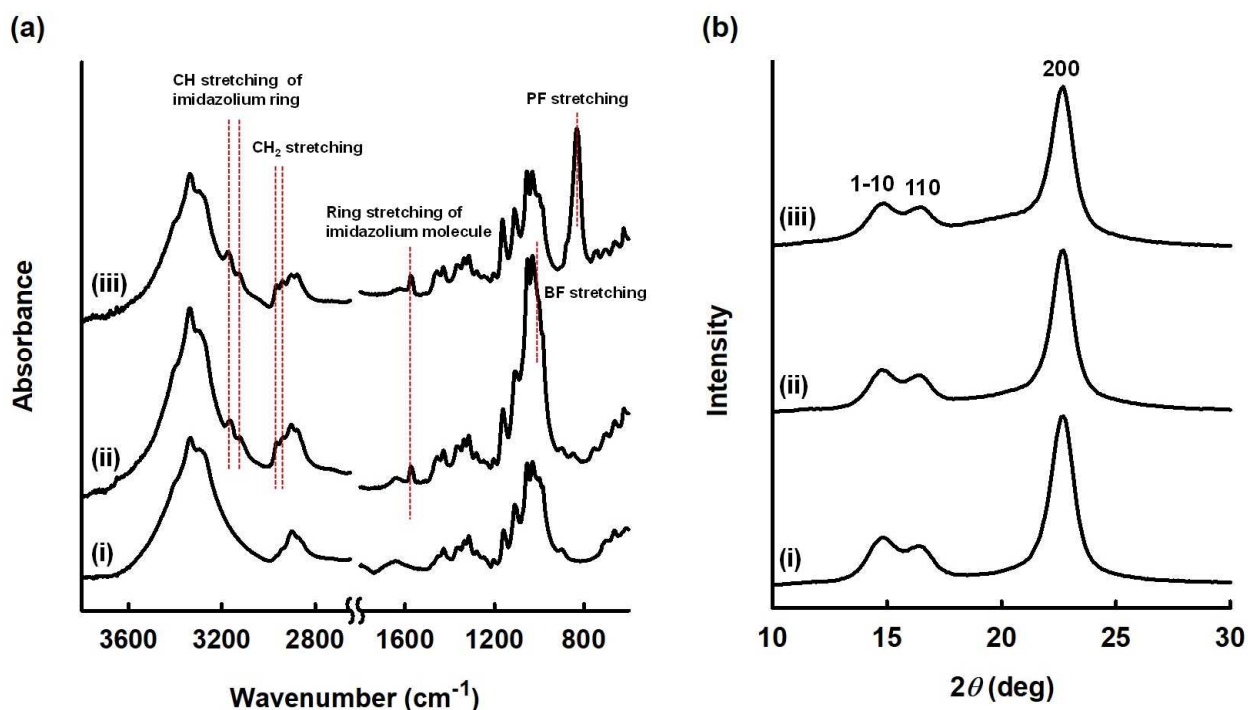


Figure S3. Characterization of cellulose filter paper before and after supporting of [bmim]BF₄ or [bmim]PF₆. (a) FT-IR/ATR spectra and (b) XRD patterns of cellulose paper (i) before and after treatment with (ii) [bmim]BF₄ and (iii) [bmim]PF₆.

As with [bmim]NTf₂ (Figure 3), FT-IR/ATR analysis confirmed the characteristic peaks of [bmim]BF₄ or [bmim]PF₆^{1,2} (Figure S3a), indicating the existence of [bmim]BF₄ or [bmim]PF₆ on the cellulose pulp fibers. As shown in Figure S3b, there was no significant change in the crystal structure of native cellulose (cellulose I)³ even after treatment with [bmim]BF₄ or [bmim]PF₆. Then, the crystallinity index of cellulose I was slightly decreased from ca. 90% to 88% or 81% after treatment with [bmim]BF₄ or [bmim]PF₆, respectively. These results suggested that [bmim]BF₄ or [bmim]PF₆ were supported on the surfaces of cellulose fibers without large changes in the crystal structure of cellulose I.

Table S1. Ionic liquid content, and electrical and physical properties of the [bmim]BF₄@paper and [bmim]PF₆@paper

	Ionic liquid content (mmol g-cellulose ⁻¹)	Volume resistivity ($\Omega \cdot \text{cm}$)	Young's modulus (GPa)	Tensile strength (MPa)
[Bmim]BF ₄ @paper	2.39 ± 0.09	1.9×10^3	0.13 ± 0.04	2.39 ± 0.49
[Bmim]PF ₆ @paper	2.17 ± 0.08	5.2×10^3	0.22 ± 0.06	3.02 ± 0.22

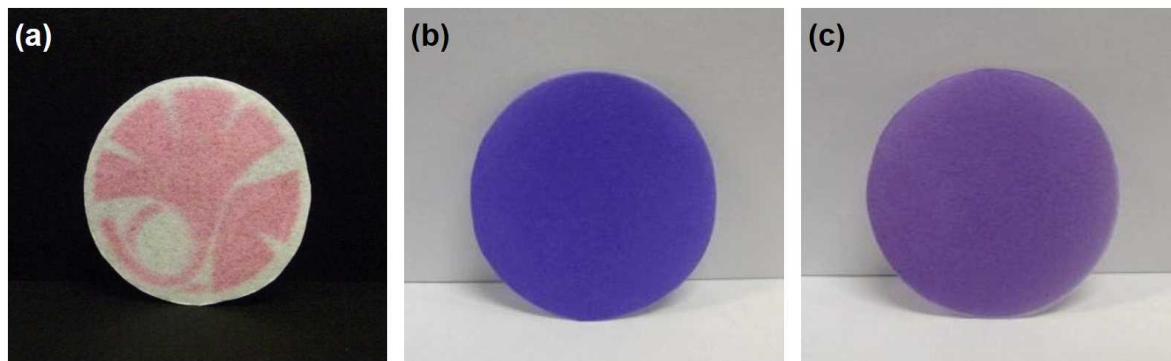


Figure S4. Photochromic paper display. (a) Photo-patterned pink coloration of the 1,2-bis[2-methylbenzo[*b*]thiophen-3-yl]-3,3,4,4,5,5-hexafluoro-1-cyclopentene/[bmim]NTf₂@paper using black masking paper, (b) blue coloration of the 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene/[bmim]NTf₂@paper, (c) purple coloration of the 1,2-bis[2-methylbenzo[*b*]thiophen-3-yl]-3,3,4,4,5,5-hexafluoro-1-cyclopentene and 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene/[bmim]NTf₂@paper. Paper size: 33 mm in diameter. Total diarylethene content: ca. 11 μmol . [Bmim]NTf₂ content: ca. 0.2 mmol. UV light: wavelength of 312 nm, light intensity of 110 $\mu\text{W cm}^{-2}$, irradiation time of 20 s.

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